

The Infrared Spectrum of Matrix Isolated BaO_2^*

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The infrared spectra of matrix isolated BaO_2 have been observed and assigned. Ba atoms were allowed to react with an argon oxygen mixture and condensed on a liquid hydrogen cooled surface. Spectra observed using $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ confirm this assignment.

Key words: Barium; barium oxides; high temperature; infrared; matrix isolations.

1. Introduction

The reaction of O_2 with barium in the gas phase has been studied by several workers [1, 2].¹ This reaction is thought to go through an intermediate BaO_2 (1), even though mass spectrometric evidence for this species is not available. Because of the importance of such an intermediate species, particularly in connection with the recent use of barium releases in the atmosphere to form BaO and Ba clouds, it was decided to study the products of this reaction using matrix isolation techniques.

2. Experimental Procedure

A beam of barium atoms was evaporated from either a stainless steel Knudsen cell or a heated stainless steel small-diameter tube and allowed to codeposit with O_2/Ar onto a liquid hydrogen cooled CsI window. The electron beam furnace used for heating the Knudsen cell, the Air Products Cryotip and the Perkin Elmer 301 spectrophotometer² have been described previously [3]. In other experiments a Beckmann IR-7 spectrophotometer with a CsI interchange and a conventional cryostat were used. Higher resolution spectra were obtained using a Perkin-Elmer 99G monochromator equipped with interference filters and suitable diffraction gratings. A chromel-alumel thermocouple inserted into a 0.030'' diameter hole drilled halfway up the wall of the Knudsen cell, was used to measure the temperature of the effusing gas. The recent vapor pressure data of Hinnov and Ohlendorf for barium were utilized [4]. A vapor pressure of barium of about 10^{-3} torr was allowed to effuse through

a 2 mm orifice in the Knudsen cell. This atomic beam was then reacted with an O_2/Ar mixture and the products of this reaction were condensed on the liquid hydrogen cooled CsI window. Deposition times varied from 3 to 37 h. Essentially identical experiments were also done with the barium beam from the resistively heated steel tube.

3. Results and Discussion

Initial results obtained by codepositing barium at a vapor pressure of about 10^{-3} torr with an argon oxygen mixture indicated a prominent absorption band in the region of 570 cm^{-1} . The multiplet structure of this band as shown in figure 1 varies with concentration of

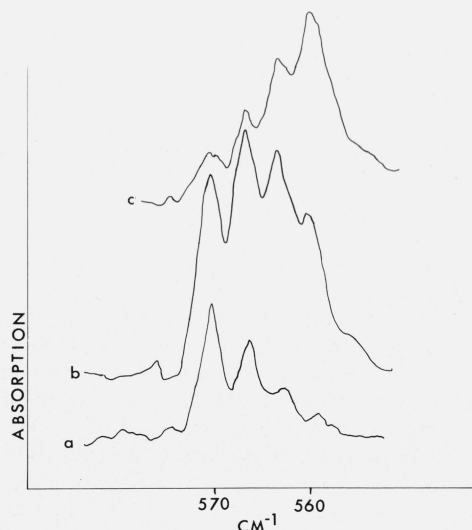


FIGURE 1. The infrared spectra of $\text{Ba} + \text{O}_2/\text{Ar}$.

(a), $\text{O}_2/\text{Ar} = 1/300$ (b), $\text{O}_2/\text{Ar} = 1/100$ (c), $\text{O}_2/\text{Ar} = 1/50$.

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¹ Figures in brackets indicate the literature references at the end of this paper.

² Certain commercial instruments are identified in this paper to specify completely the experimental procedure. In no case does such identification imply a recommendation or endorsement by the National Bureau of Standards.

oxygen to argon. (Scan (a) is for a 1/300 O₂/Ar concentration while scan (b) and (c) are for concentrations of 1/100 and 1/50 respectively.) This indicates that these multiplet structures are not due to isotopic effects (barium has five naturally occurring isotopes with abundances greater than 2%). They could possibly be due to molecular complexes with oxygen neighbors, since the oxygen concentration is about 10 times that of the barium in the matrix. Alternatively they could be ascribed to a matrix effect which is concentration dependent. In any event the feature at 570 cm⁻¹ certainly becomes more prominent as the concentration of Ar/O₂ and Ba/O₂ increases.

The reaction of Ba + ¹⁸O₂ was then studied. The spectrum shown in figure 2(b) is for about an ¹⁸O₂/Ar

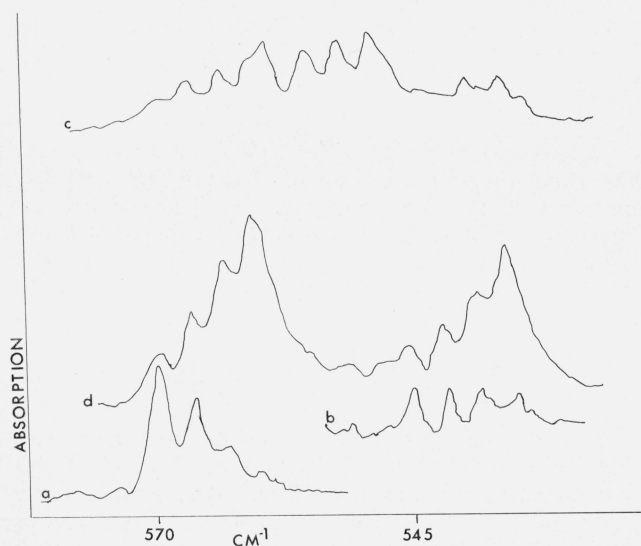


FIGURE 2. The infrared spectra of Ba + O₂/Ar.

(a), ¹⁶O₂/Ar = 1/300 (b), ¹⁸O₂/Ar = 1/200 (c), (¹⁶O₂ + ¹⁸O₂ + ¹⁶O¹⁸O)/Ar
(d), (¹⁶O₂ + ¹⁸O₂)/Ar = 1/50.

of 1/200. The same number of features were observed as in the ¹⁶O₂/Ar experiments. The relative intensities of these features are comparable to similar concentrations of ¹⁶O₂/Ar. It is perhaps interesting that the ratio of the frequencies of the corresponding features for ¹⁶O₂ and ¹⁸O₂ are the same within the experimental error for all four of the observed features for each species. Curve (a) is for ¹⁶O₂/Ar of 1/300 and is shown for comparison purposes. Curve (c) shows a Ba + ¹⁶O₂ + ¹⁸O₂ experiment. In this experiment the ¹⁶O₂ and ¹⁸O₂ were at a concentration of 1/100 yielding a total O₂/Ar of 1/50. It is seen from this experiment that the observed spectrum (d) is a superposition of spectra (a) and (b) neglecting relative intensities of the various features within each of the two multiplets. There is no absorption between or midway between corresponding pairs of bands indicating all these features are due to one oxygen molecule per species.

In spectrum (c) Ba has been codeposited with ¹⁶O₂ + ¹⁶O¹⁸O + ¹⁸O₂. The ratio of the ¹⁶O₂/¹⁸O₂ in the sample, which was then discharged electrically with a Tesla coil to scramble the oxygen sample, was about 2/1. The observed spectra contains all the features which are found in spectrum (d). In addition to these features there are lines in between which correspond on a one to one basis with those due to ¹⁶O₂ and ¹⁸O₂. These lines are about midway between the oxygen 16 and 18 lines.

It was then decided to try to obtain spectra of Ba + O₂ with about equal concentrations of both in the matrix. Figure 3 shows such spectra. The barium was heated resistively in a stainless steel tube with about a 5 mm orifice yielding roughly 6 times the barium (at the same pressure) as the Knudsen cell. Also the orifice was closer to the CsI low temperature surface. In these experiments only one prominent feature is found for Ba + ¹⁶O₂ and Ba + ¹⁸O₂ at 570 and 545 cm⁻¹ respectively (an ¹⁶O¹⁸O impurity is present in the ¹⁸O₂). An experiment with the scrambled isotopic constitution shows features at 570 and 545 cm⁻¹ and another at 559 cm⁻¹ due to Ba¹⁶O¹⁸O. This result verifies our initial results indicating that the species responsible for this absorption has two oxygen atoms or one O₂ unit per barium atom. While definitive spectroscopic proof of one barium atom per molecule has not been obtained in this study, any other conclusion doesn't seem warranted. Mass spectral, Knudsen, and optical data indicate that barium evaporates as an atom. Also the only group II diatomic molecule spectroscopically found to date is Mg₂ [5] which has a dissociation energy of about 400 cm⁻¹. Reports in the Russian literature [6] purporting to show the existence of Ca₂ are most probably misinterpreted. More likely emitters for the species are thought to be either CaC or CaN because of the ω_e, B_e and extrapolated D_e values reported.

Rather long extensive runs of 36–40 h duration were necessary to produce the spectra shown in figure 4. This is the region of O—O stretching mode for a proposed BaO₂ molecule. This mode is found at 1066 cm⁻¹ for the Ba¹⁶O₂ and at 1004 cm⁻¹ for Ba¹⁸O₂. These spectra as those shown in figure 3 were obtained with the Perkin-Elmer 99G monochromator. Unfortunately it was not possible to obtain spectra of the mixed isotope in this region (because of the large amount of sample needed). Attempts at longer runs were unsuccessful because of loss of thermal contact between the liquid hydrogen surface and the cryostat's low temperature window, or increased scattering of the argon/O₂/Ba film. The results and assignment for the BaO₂ species are summarized in table 1.

TABLE 1. Observed fundamental modes for BaO₂ (cm⁻¹)

Assignment.....	Ba ¹⁶ O ₂	Ba ¹⁸ O ₂	Ba ¹⁶ O ¹⁸ O
Ba—D Stretch.....	570	545	559
O—O Stretch.....	1066	1004	

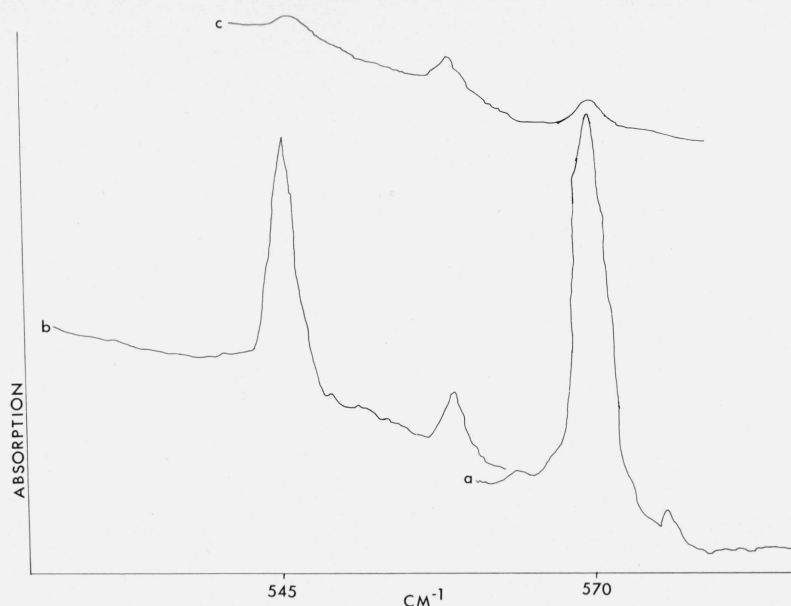


FIGURE 3. The infrared spectra of Ba + O₂/Ar with Ba/O₂ about 1:1.

(a), ¹⁶O₂/Ar = 1/100 (b), ¹⁸O₂/Ar = 1/100 (c), (¹⁶O₂ + ¹⁶O¹⁸O + ¹⁸O₂)/Ar = 1/100.

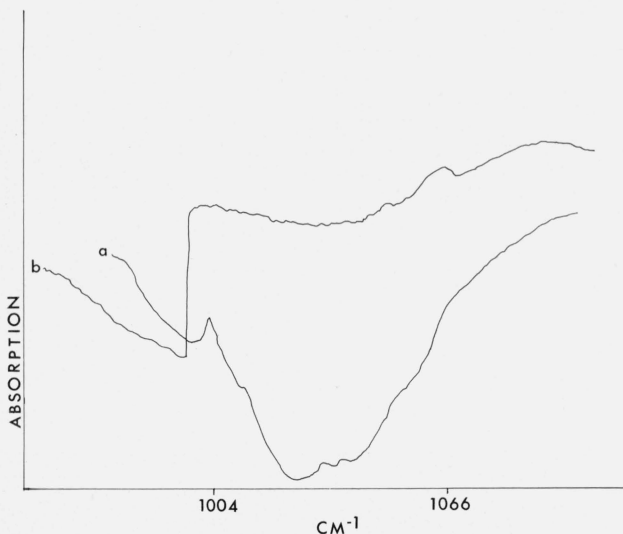
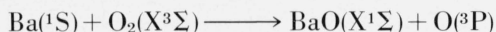


FIGURE 4. The infrared spectra of Ba + O₂/Ar with Ba/O₂ about 1:1. (The break in curve b is due to a slit change).

(a), ¹⁶O₂/Ar = 1/100 (b), ¹⁸O₂/Ar = 1/100.

4. Conclusions

The product of the reaction of barium atoms and oxygen can be trapped out in an argon matrix at liquid hydrogen temperatures. Isotopic results using ¹⁸O₂ and ¹⁶O¹⁸O in addition to ¹⁶O₂ confirm the existence of such a species, namely BaO₂. Despite the fact that the reaction



is exothermic to the extent of about 0.6 eV, no BaO was observed in these experiments. The Ba¹⁶O fundamental was recently found at 632 cm⁻¹ in an argon matrix by Linevsky [7].

The intensity of the O—O stretching mode (at 1066 cm⁻¹) is very weak compared to the Ba—O stretching mode found at 570 cm⁻¹ for Ba¹⁶O₂. This low intensity coupled with a frequency which is similar to the O₂⁻ fundamental frequency reported on by several workers found in solids such as O₂⁻ doped alkali halide single crystals [8, 9] tends to support a charge transfer type structure consisting of Ba⁺ + O₂⁻. A completely ionic model would yield an O—O bond which would indeed not be infrared active. Crude attempts by us to observe fluorescence spectra of the O₂⁻ by using Hg 2537 Å line were not successful possibly because of the low fluorescence yield or scattering matrix.

Unfortunately the other BaO stretching mode has not been observed as yet. It is not at all clear why the intensity of this mode is weak compared to the other BaO stretching mode. Weak features have been found in the Ba¹⁶O₂ spectra; however, comparable bands in the Ba¹⁸O₂ have not been found. Without these data it is not possible to assign the 570 and 545 cm⁻¹ in Ba¹⁶O₂ and Ba¹⁸O₂ to the symmetric or asymmetric stretching frequencies of BaO₂.

5. References

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